

(19)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11) Publication number:

**0 548 504 A2**

(12)

**EUROPEAN PATENT APPLICATION**

(21) Application number: 92118561.7

(51) Int. Cl.<sup>5</sup>: **C01B 33/037, C01B 21/46,  
H01L 21/306**

(22) Date of filing: 29.10.92

(30) Priority: 29.10.91 JP 308268/91  
31.10.91 JP 311484/91(43) Date of publication of application:  
30.06.93 Bulletin 93/26(84) Designated Contracting States:  
BE DE FR GB IT NL(71) Applicant: **HI-SILICON Co., Ltd.**  
5, Mita-cho  
Yokkaichi-shi, Mie-ken(JP)(72) Inventor: Ito, Hideo  
c/o 5, Mita-cho  
Yokkaichi-shi, Mie-ken(JP)  
Inventor: Narukawa, Mitsutoshi  
c/o 5, Mita-cho  
Yokkaichi-shi, Mie-ken(JP)  
Inventor: Sakai, Kazuhiro  
c/o 5, Mita-cho  
Yokkaichi-shi, Mie-ken(JP)(74) Representative: **Strehl, Schübel-Hopf,  
Groening**  
Maximilianstrasse 54 Postfach 22 14 55  
W-8000 München 22 (DE)(54) **Process for cleaning silicon mass.**

(57) In a process for cleaning a silicon mass with an acid washing solution, a waste solution containing a mixed acid composed of nitric acid and hydrofluoric acid is introduced to a distillation step, and hydrofluoric acid is introduced to a distillation cooling portion to prevent precipitation of silicon dioxide. The waste cleaning liquor is distilled to recover nitric acid.

In a process for cleaning a silicon mass by acid-washing with a cleaning solution containing a mixed acid composed of nitric acid and hydrofluoric acid, the cleaned silicon mass is retained in steam of high purity after acid-washing so that acid remaining on the surface of said cleaned silicon mass can be rinsed and removed with condensed water formed on the surface of said silicon mass.

**EP 0 548 504 A2**

Background of the Invention

## 1. Field of the Invention

5 The present invention relates to improvement in the process for cleaning a silicon mass such as a polycrystalline silicon mass with an acid. More particularly, the present invention relates to a process for cleaning a silicon mass in which nitric acid is effectively recovered for reuse from the waste solution of a treatment solution which is used as a cleaning solution or an etchant and comprised mainly of a mixed acid composed of nitric acid and hydrofluoric acid, as well as to a process for removing such an acid adhering to  
 10 a silicon mass, more specifically a process for cleaning a silicon mass, particularly a polycrystalline silicon mass, in which the silicon mass is etched with such an acid and then the acid adhering to the silicon mass is removed rapidly.

## 2. Description of the Prior Art

15 A treatment solution comprised mainly of fluoro-nitric acid, which is a mixture of nitric acid and hydrofluoric acid has heretofore been used as a cleaning liquid or an etchant for a polycrystalline silicon mass or a silicon wafer. In the conventional acid-washing processes, the treatment solution which contains impurities at high concentrations and is thus no more usable is disposed of as a waste. However, the waste  
 20 treatment solution still contains nitric acid in an amount of 40 to 50% by weight and is a high concentration, strongly acidic solution, and hence the waste disposal must be subjected to a neutralization treatment or the like which incurs unnegligible cost. The waste disposal arises a severer problem according as the amount of silicon to be treated increases. Therefore, it is desired to recover nitric acid and the like from the waste treatment solution to decrease cost incurred in the waste disposal and reuse nitric acid.

25 Despite attempts to recover nitric acid from the waste solution produced and reuse it in the process of cleaning silicon, it has been difficult to recover nitric acid effectively. For example, for the surface treatment of stainless steel plates, there have been known several processes for recovering acids from a waste acid solution containing a mixed acid composed of nitric acid and hydrofluoric acid by distillation (Japanese Patent Publication No. 11755/1981, etc.). In actuality, when attempts were made to separate the waste acid  
 30 by distillation according to the conventional processes, the piping would be clogged to make it difficult to continue the distillation so that the separation and recovery of nitric acid, etc., are difficult in the case where the waste solution from the silicon treatment process is handled.

In addition to the problem of disposal of the waste cleaning solution, the acid-washing of a silicon mass has a problem in rinsing after the acid-washing as described below. For example, in the production of a  
 35 highly pure polycrystalline silicon, the cleaning is carried out after the silicon is grown in the form of a rod, and cut or crushed to an appropriate size to form a cylindrical mass (referred to as "chunk") or a small mass (referred to as "lump"). As already stated, the cleaning is performed by etching the silicon mass with an etchant comprised mainly of hydrofluoric acid and nitric acid to remove impurities adhering to and an oxide coating formed on the surface of the silicon mass, and then rinsing the remaining etchant with purified  
 40 water. Thereafter, the cleaned silicon mass is transferred to a drying step.

Since the etchant is a strongly acidic solution, it is necessary to remove the solution as completely as possible in order to obtain a clean silicon mass. However, the silicon mass obtained as described above has a complicated surface structure having minute hollow portions as viewed on a microscopic scale so that the acid used as the etchant spreads in the hollow portions. As a result, mere spraying of water onto the  
 45 surface of the silicon mass is insufficient for the acid which has permeated or adhered to the surface of the silicon mass to be removed completely. For this reason, the silicon mass is immersed in a purified water bath to remove the acid as completely as possible.

Although this process is advantageous in that it is simple, it takes a long time in the cleaning step. At present, the silicon mass must be immersed for one night while exchanging rinsing water several times to  
 50 decrease the amount of nitric acid ion which remains after the cleaning treatment to an acceptable level for practical use. In the immersion cleaning process, not only a large space is required for an immersion bath but also production of a large amount of purified water and recovery thereof are necessary. Furthermore, in the process, the acid is removed by spontaneous diffusion, and hence it is often the case that the removal of the acid is incomplete depending on the condition of the surface of the silicon mass. Therefore, there has  
 55 been a keen desire for rationalize the process by enabling the removal of acid with a smaller amount of purified water and in a shorter time.

Summary of the Invention

The present invention is to solve the aforementioned problems and provides a process for effectively recovering nitric acid from a waste cleaning solution for reuse.

Also, the present invention provides a process for acid-washing a silicon mass, in which the acid adhering to the silicon mass after the acid-washing is removed rapidly.

Specifically, according to one aspect of the present invention, there is provided a process for cleaning a silicon mass by acid-washing with a cleaning solution containing a mixed acid composed of nitric acid and hydrofluoric acid, comprising the steps of: introducing a waste cleaning solution (in the following often referred to as "waste solution") to a distillation step after washing with said cleaning solution; introducing hydrofluoric acid to a distillation cooling portion to prevent precipitation of silicon dioxide; and distilling the waste cleaning liquor to recover the nitric acid

In a preferred embodiment of the aforementioned process of the present invention, the nitric acid recovered from the waste solution may be added to the cleaning solution for reuse.

In another preferred embodiment of the aforementioned process of the present invention, the waste solution may be continuously distilled while continuously flowing a small amount of hydrofluoric acid into the distillation cooling portion.

In a still another preferred embodiment of the aforementioned process of the present invention, after the acid-washing, a waste solution is introduced to a distillation step, and the silicon mass cleaned may be retained in steam of high purity so that acid remaining on the surface of the silicon mass can be rinsed and removed with condensed water formed on the surface of the silicon mass.

According to another aspect of the present invention, there is provided a process for cleaning a silicon mass by acid-washing with a cleaning solution containing a mixed acid composed of nitric acid and hydrofluoric acid, comprising the step of: retaining in steam of high purity a cleaned silicon mass after acid-washing so that acid remaining on the surface of the cleaned silicon mass can be rinsed and removed with condensed water formed on the surface of the silicon mass.

In the present invention, the cause of the clogging of the piping upon distilling a waste silicon cleaning liquor was analyzed, and it has now been found that soluble silicon compound present in the waste silicon etching solution as a result of the cleaning of silicon or etching is thermally decomposed upon distillation to produce silicon tetrafluoride ( $\text{SiF}_4$ ), which is distilled off together with nitric acid and hydrofluoric acid and reacts with moisture in a distillation condensing portion to precipitate silicon dioxide, this clogging the piping. Incidentally, the silicon compound dissolved in the waste cleaning solution is mainly hydrosilicofluoric acid ( $\text{H}_2\text{SiF}_6$ ) and contains a smaller amount of silicon fluoride. The silicon etching solution is a fluoro-nitric acid solution composed of nitric acid and hydrofluoric acid and presence of a small amount of silicon therein causes no problem for etching the silicon mass. Accordingly, if silicon dioxide precipitated in the distillate is dissolved with hydrofluoric acid, the distillate containing the resulting solution of silicon dioxide may be added as it is to the silicon etching solution for reuse. Therefore, continuous distillation can be realized by flowing a small amount of hydrofluoric acid to the condensing portion. Hydrofluoric acid contained in the silicon etchant is mostly consumed in the etching-cleaning of silicon to form hydrosilicofluoric acid ( $\text{H}_2\text{SiF}_6$ ), and at a lower temperature region hydrofluoric acid component is distilled out together with silicon dioxide. Therefore, in batch treatments, high purity nitric acid containing only a small amount of hydrofluoric acid and other impurities can be recovered effectively if the initial distillates are discarded since silicon dioxide and hydrofluoric acid are mainly distilled out at initial stages of distillation.

On the other hand, the present inventors tried to improve the washing step for rinsing acidic solution remaining on the silicon mass, and investigated various processes such as a process in which a silicon mass is repeatedly immersed in a plurality of cleaning baths, a process in which hot water is used in the cleaning bath, and a process in which ultrasonic cleaning is performed in the cleaning bath. However, none of these processes investigated showed any significant improvement. As a result of further investigation, it has now been found that quite unexpectedly, preheating with steam as a pretreatment to be followed by a drying step was successful in efficiently removing the acid in a short time. The present invention is based on this discovery.

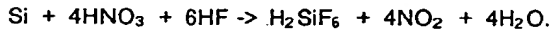
Brief Description of the Drawing

Fig. 1 is a schematic cross sectional view showing a distillation vessel for practicing the process of the present invention.

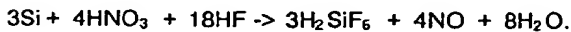
Detailed Description of the Invention

## (1) Distillation Step of a Waste Solution

Fluoro-nitric acid solution used as a cleaning solution or an etchant for silicon contains 40 to 60 % by weight of nitric acid and 2 to 30 % by weight of hydrofluoric acid. In the reaction of etching a silicon mass, Si reacts with nitric acid ( $\text{HNO}_3$ ) and hydrofluoric acid ( $\text{HF}$ ) to produce hydrosilicofluoric acid ( $\text{H}_2\text{SiF}_6$ ), nitrogen dioxide ( $\text{NO}_2$ ) and water ( $\text{H}_2\text{O}$ ) as follows:



On the other hand, silicon (Si) reacts with nitric acid ( $\text{HNO}_3$ ) and hydrofluoric acid ( $\text{HF}$ ) to produce hydrosilicofluoric acid ( $\text{H}_2\text{SiF}_6$ ), nitrogen monoxide ( $\text{NO}$ ) and water ( $\text{H}_2\text{O}$ ) as follows:



As will be understood from the above reaction schemes, the amount of hydrofluoric acid consumed is larger than that of nitric acid, and in addition, hydrofluoric acid is more expensive than nitric acid. Therefore, in usual acid washing step or cleaning steps, the etching solution is used repeatedly until the concentration of impurities increases so high as to exceed acceptable level for use while replenishing hydrofluoric acid. For example, the etching solution is disposed of as a waste solution when the concentration of impurities in the solution has reached about 1 ppm. The waste solution, which has almost no etching effect against Si, contains about 40 to 50 % by weight of nitric acid. The waste solution also contains 1 to 20 % by weight of hydrosilicofluoric acid ( $\text{H}_2\text{SiF}_6$ ).

The process of the present invention is to distil the waste solution and recover nitric acid therefrom. Fig. 1 shows an example of a distillation apparatus which can be used in the process of the present invention. In Fig. 1, the distillation apparatus includes an oil bath 10 in which a waste solution bottle 11 is arranged. A branched pipe 12 is connected to an upper end of the waste bottle 11. A cooling portion 13 is formed near one end 12a of the branched pipe 12 which end opens in a collecting vessel 14 for collecting a distillate. The other end 12b of the branched pipe 12 is connected to a feed pipe 15 for feeding hydrofluoric acid so that hydrofluoric acid is flown to the cooling portion 13 through the feed pipe 15.

When the waste solution is heated for distillation to a temperature higher than the boiling points of hydrofluoric acid and nitric acid, i.e., about  $110^\circ\text{C}$  and about  $121^\circ\text{C}$ , respectively, usually  $100$  to  $125^\circ\text{C}$ , first a water-hydrofluoric acid system distills out at a lower temperature region. Here, hydrofluoric acid in the waste solution is dissolved therein in the form of hydrosilicofluoric acid ( $\text{H}_2\text{SiF}_6$ ), and this compound upon the heating of the waste solution is decomposed to silicon fluoride, which has a boiling point not exceeding  $0^\circ\text{C}$ . Silicon fluoride distills together with hydrofluoric acid and reacts with moisture to form silicon dioxide which precipitates in the cooling portion. Hence, hydrofluoric acid is passed through the cooling portion 13 to dissolve therewith silicon dioxide which precipitated there in order to remove it. Hydrofluoric acid may be fed in the form of a liquid which flows down or sprayed as a shower in the cooling portion 13. Silicon dioxide is dissolved in hydrofluoric acid and washed out from the cooling portion 13.

In operating the aforementioned distillation apparatus, hydrofluoric acid may be fed when the precipitation of silicon dioxide is observed. Upon the feeding of hydrofluoric acid, silicon dioxide precipitate is dissolved and removed in a few minutes. When the process of the present invention is practiced on an industrial scale, the timing when the addition of hydrofluoric acid is to be started and the amount of hydrofluoric acid to be added may be set up depending on the concentration of hydrosilicofluoric acid. In the case of batch distillation, silicon dioxide precipitates at an initial stage of distillation but no precipitation occurs in a later stage. When the waste solution is to be distilled continuously, the distillation is performed while flowing down a small amount of hydrofluoric acid.

As described above, in the distillation of the waste solution, a water-hydrofluoric acid system distills at a lower temperature region. Since much of hydrofluoric acid is dissolved in the waste solution in the form of hydrosilicofluoric acid, in the case of batch distillation hydrofluoric acid distills out simultaneously with the precipitation of silicon dioxide at the initial stage of distillation, and then mainly a nitric acid-water system distills out, thus the concentration of nitric acid increasing gradually. The precipitation of silicon dioxide is decomposed by hydrofluoric acid flowed down. Excepting the initial distillate in which silicon dioxide is dissolved, subsequently obtained nitric acid fractions are collected. Metallic impurities other than silicon contained in the etching solution remain in the waste solution. In this case, the use of a distillation system made of Teflon (polytetrafluoroethylene) makes it possible to recover high purity nitric acid with no

contamination in the distillation system. For example, when a mixed acid composed of nitric acid and hydrofluoric acid which is commercially available and has an electronic industry grade is used as a cleaning solution for polycrystalline silicon, and the resulting waste solution is distilled by the process of the present invention, nitric acid of a considerably high purity can be obtained; the concentration of impurities in the nitric acid recovered is by about 1/10 time as high as that of the impurities in the commercially available nitric acid solution.

Since the washing solution is a mixed acid composed of hydrofluoric acid and nitric acid, if a small amount of silicon is present therein, such silicon does not serve as a contaminant in the etching or cleaning of silicon, and thus in order to reuse it the distillate can be added as it is without removing initial distillate to a fresh washing solution replenished with hydrofluoric acid. Therefore, a waste solution can be continuously reused by continuously distilling it while flowing a small amount of hydrofluoric acid through the cooling portion and adding recovered nitric acid to a fresh washing solution.

An example of continuous distillation is performed at a temperature of 120 to 125°C in a distillation apparatus having a similar arrangement as shown in Fig. 1 but differing in that a branching portion is provided each at a lower boiling point region where mainly a water-hydrofluoric acid system distills and at a higher boiling point region where mainly a water-nitric acid system distills in a midway between the waste liquor bottle 10 and the cooling portion 13, with nitric acid being continuously recovered from the branching portion at the higher boiling point region. In this case, a mixed acid of fluoro-nitric acid is obtained. As another example, at least two distillation apparatuses are used. The first distillation vessel is heated at 110 to 120°C to distil out a lower boiling point portion comprised mainly of hydrofluoric acid, and the residue in the first distillation vessel is introduced into the second distillation vessel which is heated to 120 to 125°C to distil out a higher boiling point portion comprised mainly of nitric acid. In this case, silicon fluoride has already been separated in the first distillation step and no need for flowing down hydrofluoric acid through the cooling portion, resulting in that nitric acid fractions containing much less hydrofluoric acid component can be obtained. According to a still another example of continuous distillation using two distillation apparatuses, distillation may be carried out as follows. That is, the first distillation vessel is heated to 120 to 125°C to distil out hydrofluoric acid and nitric acid, and then the distillate is introduced into the second distillation vessel which is heated to 100 to 110°C to distil out hydrofluoric acid, a lower boiling point component, and nitric acid as a residue is recovered.

## (2) Rinsing Step After Acid-Washing

The silicon mass cleaned in the aforementioned cleaning step is retained in steam in high purity to condense water on the surface of the silicon mass to wash and remove acid remaining on the surface of the silicon mass with the condensed water.

Steam of purified water is generated by heating purified water by a conventional method. The steam is fed in such an amount that steam is condensed on the surface of the silicon mass and condensed water is renewed by turns. For example, when a silicon mass at ambient temperature is conveyed in steam at 100°C at atmospheric pressure, it is sufficient to generate steam in an amount of about 0.5 g/minute per unit volume (liter) of steam chamber. The temperature of steam is usually about the boiling point of water in the system concerned. The pressure of steam is not limited particularly but a pressure of about one to several times as high as the outer pressure is preferred in order to simplify the arrangement of the apparatus. So far as the quality of the silicon mass is not deteriorated, high temperature or high pressure steam may be used.

The manner in which the silicon mass is retained in steam is not limited particularly. It may be retained in a chamber filled with steam or steam may be blown onto the silicon mass under the conditions that the whole surface of the silicon mass is covered by the steam. Preferably, the silicon mass is retained in a stream of steam so that the condensation of steam proceeds rapidly. The silicon mass may be retained on a net or a cage made of a material which is not a source of contamination to silicon.

While it varies depending on the absolute amount of the residual acid and the shape of the silicon mass, the retention time may as a rough measure be as long as the surface of the silicon mass is wetted with condensed water. Usually, the retention time is on the order of several minutes, and is drastically shortened as compared with the conventional immersion cleaning process.

In the process of the present invention, steam of purified water condenses on the silicon mass and the residual acid on the surface thereof migrates into the condensed water and then the condensed water having dissolved therein the acid is removed from the silicon. It is essential that these steps are carried out in order, and it should be noted that the temperature, flow rate of steam, retention time, etc. are determined depending on whether such steps are achieved or not. Although it is unclear what a mechanism the effect

of the present invention is ascribable to, it would be possible that steam (water) molecules permeate into fine surface structure such as unevenness or cracks on the surface of the silicon mass and dissolves the acid adhering to the structure; the heat generated when steam condensed causes the surface of the silicon mass and gases staying thereon to expand locally to facilitate the removal of acids; and so on. However, as will be apparent from the comparison between examples and comparative examples described later on, the effect of the present invention is remarkable since the removal of acid is achieved in a few minutes in the present invention.

The rinsing step may be performed in combination with a prerinsing step. More specifically, it is preferred to carry out prerinsing prior to the rinsing process described above. In this case, the cleaning with steam is performed after drying to such an extent that the effect of the present invention is not harmed. Postcleaning may be performed in order to wash the condensed water off. Remarkable effects can be achieved by performing the rinsing step in combination with a prerinsing step.

#### Advantages of the Present Invention

When nitric acid is to be recovered by distilling a waste solution, it has been often difficult to recover nitric acid since clogging of the distillation system occurs. On the contrary, according to the present invention, the clogging of the distillation system is solved and nitric acid can be recovered efficiently. The concentration of impurities contained in nitric acid to be recovered by the process of the present invention is lower than commercially available nitric acid, and thus nitric acid of high purity can be obtained according to the invention.

Also, according to the process of the present invention, the removal of acids can be achieved in a few minutes, resulting in reduction in time required for cleaning a silicon mass. In addition, the process of the present invention is economically advantageous since the use of a large amount of water for immersion is unnecessary, which minimizes the amount of purified water to be used and reduces the space required for arranging an immersion bath. Furthermore, according to the process of the present invention, the silicon mass is contacted with steam and its temperature increases thereby, resulting in that the time of drying in the subsequent step can also be shortened.

#### Examples

Hereinafter, the present invention will be described in more detail by examples. However, the present invention should not be construed as being limited thereto.

##### Example 1

The distillation apparatus shown in Fig. 1 having a distillation vessel 11 in the form of a 6-liter Teflon bottle to which was connected a Teflon branching pipe 12 was used. Five (5) liters of a waste silicon cleaning liquor (nitric acid: 45 % by weight, hydrofluoric acid: 0.5 % by weight, hydrosilicofluoric acid: 6 % by weight) were charged in the distillation vessel and heated to 100 °C to initiate distillation. Immediately after the initiation of distillation, white solids began to precipitate on the inner wall of the cooling portion 13, and hydrofluoric acid was flown down through the pipe 15 to the cooling portion 13 at a rate of 40 ml/minute for 40 minutes. As a result, the solids on the inner wall of the pipe were dissolved rapidly. The distillation was continued while stopping the supply of hydrofluoric acid from time to time and observing the state of precipitation of the solids. When 1.5 liters of the distillate accumulated, no more precipitation of the solids was observed, and the supply of hydrofluoric acid was stopped. After discarding initial distillates, the distillation was continued for additional 25 hours to obtain 3 liters of nitric acid.

Nitric acid was recovered in the same manner as described above from various samples. The concentrations of metallic impurities in the nitric acid obtained were as shown in Table 1. As shown in Table 1, the concentration of impurities in the nitric acid recovered was much lower than commercially available nitric acid of an electronic industry grade. Thus, nitric acid of high purity was recovered.

At least two distillation apparatuses of the same type as described above were used. The first distillation vessel was heated to 110 to 120 °C to distil out a lower boiling point portion comprised mainly of hydrofluoric acid, and the residue in the first distillation vessel was introduced into the second distillation vessel which was heated to 120 to 125 °C to distil out a higher boiling point portion comprised mainly of nitric acid. The distillation conditions and the amount of the impurities in the recovered nitric acid are shown in Tables 2 and 3, respectively.

Example 2

Three hundreds (300) milliliters (ml) of the recovered nitric acid obtained in Example 1 (concentration of nitric acid: 62.48 % by weight, concentration of hydrofluoric acid: 2.1 % by weight), and 300 ml of 50 % hydrofluoric acid were mixed to prepare a silicon etching solution, and etching test for silicon was conducted using the etching solution thus obtained. For comparison, etching test for silicon was conducted under the same conditions using commercially available nitric acid of an electronic industry grade to which no recovered nitric acid was added. The results obtained are shown in Table 4. As shown in Table 4, the etching solution containing the recovered nitric acid had an etching rate equal to that of the etching solution not containing the recovered nitric acid. The resistivity of the silicon measured was substantially the same. As will be apparent from the results, the recovered nitric acid was able to be reused as an etching solution.

Example 3

An acid-washing bath containing about 10 liters of an acid composition composed of 60 % nitric acid and 50 % hydrofluoric acid in a proportion of 9 : 1 and seven prerinsing baths containing each about 15 liters of purified water were provided.

A silicon lump weighing about 3 kg was placed in a cage made of a resin and the cage was immersed in the acid-washing bath for about 40 seconds and precleaned in the prerinsing baths. The prerinsing was performed by repeating a unit operation of 10 seconds' immersion followed by 5 seconds' withdrawing for 2 minutes per bath. This prerinsing operation was repeated for all the baths in order. Then, the thus prerinsed silicon lump together with the cage was placed in a commercially available stainless steel kettle filled with steam of purified water generated by charging purified water in the kettle and heating. The silicon lump was retained in steam for 5 minutes. Thereafter, condensed water was washed out with about 4 liters of purified water.

To determine the amount of nitric acid remaining on the surface of the silicon lump, the silicon lump together with the cage was immersed in 7 liters of purified water for one night. After completion of the immersion, the concentration of nitric acid ion in the immersing water was measured using a nitric acid ion electrode. Results obtained indicated it was below 0.1 ppm, a detection limit.

Comparative Example 1

A silicon lump was cleaned in the same manner as in Example 3 except that the prerinsing process was not used. The amount of acid remaining on the surface of the silicon lump was determined in the same manner as in Example 1. As a result, the concentration of nitric acid ion was 0.50 ppm.

Comparative Example 2

A silicon lump was cleaned in a conventional manner. More specifically, the cleaning procedure was performed as follows.

An acid-washing bath containing about 10 liters of an acid composition composed of 60 % nitric acid and 50 % hydrofluoric acid in a proportion of 9 : 1 and two rinsing baths containing each about 15 liters of purified water were provided.

A silicon lump weighing about 3 kg was placed in a cage made of a resin and the cage was immersed in the acid-washing bath for about 40 seconds and precleaned in the rinsing baths. The rinsing was performed by repeating a unit operation of 10 seconds' immersion followed by 5 seconds' withdrawing for 2 minutes per bath. This prerinsing operation was repeated for the both baths in order. Then, the thus prerinsed silicon lump together with the cage was immersed in 7,000 liters of purified water for one night. The purified water in the bath was wholly replaced with the same amount of fresh purified water for every 4 hours three times.

To determine the amount of nitric acid remaining on the surface of the silicon lump, the silicon lump together with the cage was immersed in 7 liters of purified water for one night. After completion of the immersion, the concentration of nitric acid ion in the immersing water was measured using a nitric acid ion electrode. Results obtained indicated it was below 0.34 ppm, a detection limit.

## Comparative Example 3

A silicon lump was cleaned in the same manner as in Example 3 except that the prerinsing process was replaced by immersion in hot water at 75 °C for 5 minutes. The amount of acid remaining on the surface of the silicon lump was determined in the same manner as in Example 3. As a result, the concentration of nitric acid ion was 0.51 ppm, and the hot water immersion gave no effect.

Table 1: Amount of Impurities in Recovered Nitric Acid  
Unit: 10<sup>-9</sup> g/ml (ng/ml: ppb)

Element	Commercially Available Nitric Acid	Recovered Nitric Acid			Distillation Residue
		Sample 1	Sample 2	Sample 3	
Al	10.0	0.8	0.7	0.9	530 - 600
B	0.6	<0.2	<0.2	<0.2	160 - 240
Ca	34.0	0.1	0.1	<0.1	4400 - 500
Cr	70.0	<0.1	<0.1	<0.1	1300 - 220
Cu	0.1	<0.1	<0.1	<0.1	1800 - 240
Fe	6.0	0.9	0.6	0.8	7300 - 8700
K	4.0	0.1	<0.1	0.1	720 - 950
Li	0.1	<0.1	<0.1	<0.1	<0.1
Mg	9.0	2.0	2.0	1.0	600 - 730
Na	300.0	20.0	30.0	20.0	3000 - 4200
Ni	0.5	<0.1	<0.1	<0.1	120 - 280
P	1.0	<1.0	<1.0	<1.0	40 - 60
Ti	100.0	20.0	20.0	20.0	1100 - 1900
Si	210 ppm	150 ppm	320 ppm	320 ppm	28 ppm



Table 2 Conditions of Continuous Distillation

Heating Temperature (°C)	First Still Pot	110 - 120
	Second Still Pot	120 - 125
Amount of Waste Liquor		10 ml/minute
Amount of Liquor Withdrawn First Still Pot		7 - 8 ml/minute
Amount of Hydrofluoric Acid Dropped to Cooling Portion		5 ml/minute

Table 3: Amount of Impurities in Nitric Acid Recovered  
by Continuous Distillation  
Unit: 10<sup>-9</sup> g/ml (ng/ml: ppb)

Recovered Nitric Acid			
Element	Sample 1	Sample 2	Sample 3
Al	1.0	1.1	0.9
B	<0.2	<0.2	<0.2
Ca	0.2	0.4	<0.2
Cr	<0.1	<0.1	<0.1
Cu	<0.1	<0.1	<0.1
Fe	1.0	1.5	1.0
K	0.2	0.1	<0.1
Li	<0.1	<0.1	<0.1
Mg	3.0	1.0	3.0
Na	50.0	60.0	30.0
Ni	<0.1	<0.1	<0.1
P	<1.0	<1.0	<1.0
Ti	5.0	3.0	6.0
Si	500 ppm	600 ppm	500 ppm

Table 4

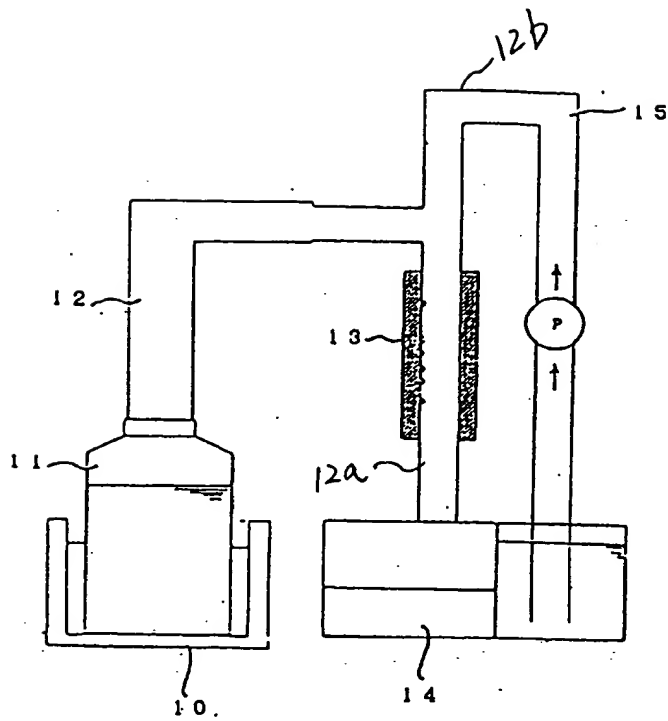
Nitric Acid Used As Etching Liquor	Silicon Etching Rate	Resistivity ( $\Omega \cdot \text{cm}$ )		
		Sample 1	Sample 2	Sample 3
Recovered Nitric Acid	13 $\mu\text{m}/\text{minute}$	2840	2520	2700
Commercially Available Nitric Acid	12 $\mu\text{m}/\text{minute}$	2820	2600	2700

## Claims

1. A process for cleaning a silicon mass by acid-washing with a cleaning solution containing a mixed acid composed of nitric acid and hydrofluoric acid, comprising the steps of:  
 introducing a waste solution to a distillation step after washing with said cleaning solution;  
 introducing hydrofluoric acid to a distillation cooling portion to prevent precipitation of silicon dioxide; and  
 distilling said waste solution to recover said nitric acid.

2. The process as claimed in claim 1, wherein said nitric acid recovered from said waste solution is added to said cleaning solution for reuse.
3. The process as claimed in claim 1, wherein said waste solution is continuously distilled while continuously flowing a small amount of hydrofluoric acid into said distillation cooling portion.
4. The process as claimed in claim 1, wherein after said acid-washing, said waste solution is introduced to a distillation step, and said silicon mass washed is retained in steam of high purity so that acid remaining on the surface of said silicon mass can be rinsed and removed with condensed water formed on the surface of said silicon mass.
5. A process for cleaning a silicon mass by acid-washing with a cleaning solution containing a mixed acid composed of nitric acid and hydrofluoric acid, comprising the step of:  
retaining in steam of high purity a cleaned silicon mass after acid-washing so that acid remaining on the surface of said cleaned silicon mass can be rinsed and removed with condensed water formed on the surface of said silicon mass.
6. The process as claimed in Claim 1, wherein after said acid-washing, said washed silicon mass is subjected to a prerinsing step in which said silicon mass is immersed in purified water, then said silicon mass is retained in steam of high purity so that acid remaining on the surface of said silicon mass can be rinsed and removed with condensed water formed on the surface of said silicon mass.

Fig. 1



(19)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11) Publication number:

**0 548 504 A3**

(12)

**EUROPEAN PATENT APPLICATION**(21) Application number: **92118561.7**(51) Int. Cl.<sup>5</sup>: **C01B 33/037, C01B 21/46,  
H01L 21/306**(22) Date of filing: **29.10.92**(30) Priority: **29.10.91 JP 308268/91  
31.10.91 JP 311484/91**(43) Date of publication of application:  
**30.06.93 Bulletin 93/26**(84) Designated Contracting States:  
**BE DE FR GB IT NL**(88) Date of deferred publication of the search report:  
**01.12.93 Bulletin 93/48**(71) Applicant: **HI-SILICON Co., Ltd.  
5, Mita-cho  
Yokkaichi-shi, Mie-ken(JP)**(72) Inventor: **Ito, Hideo  
c/o 5, Mita-cho  
Yokkaichi-shi, Mie-ken(JP)  
Inventor: Narukawa, Mitsutoshi  
c/o 5, Mita-cho  
Yokkaichi-shi, Mie-ken(JP)  
Inventor: Sakai, Kazuhiro  
c/o 5, Mita-cho  
Yokkaichi-shi, Mie-ken(JP)**(74) Representative: **Strehl Schübel-Hopf Groening  
& Partner  
Maximilianstrasse 54  
D-80538 München (DE)**(54) **Process for cleaning silicon mass.**

(57) In a process for cleaning a silicon mass with a acid washing solution, a waste solution containing a mixed acid composed of nitric acid and hydrofluoric acid is introduced to a distillation step, and hydrofluoric acid is introduced to a distillation cooling portion to prevent precipitation of silicon dioxide. The waste cleaning liquor is distilled to recover nitric acid.

In a process for cleaning a silicon mass by acid-washing with a cleaning solution containing a mixed acid composed of nitric acid and hydrofluoric acid, the cleaned silicon mass is retained in steam of high purity after acid-washing so that acid remaining on the surface of said cleaned silicon mass can be rinsed and removed with condensed water formed on the surface of said silicon mass.

**EP 0 548 504 A3**



European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number

EP 92 11 8561

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. CL.5)
A	DE-A-3 128 979 (SIEMENS) ---		C01B33/037 C01B21/46 H01L21/306
A	DE-A-3 129 009 (SIEMENS) ---		
A	US-A-2 992 080 (C.S. HERRICK) ---		
A	EP-A-0 125 630 (HELIOTRONIC FORSCHUNG UND ENTWICKLUNGSGESELLSCHAFT) ---		
A	WO-A-9 114 655 (COGEMA) ---		
Y	US-A-4 186 032 (RCA CORP.) * column 1, paragraph 3; claim 1; figure 2 *	5	
Y	RCA REVIEW vol. 31, June 1970, PRINCETON USA pages 207207 - 264 W. KERN 'RADIOCHEMICAL STUDY OF SEMICONDUCTOR SURFACE CONTAMINATION' * page 262, paragraph 2 3 * * page 231, paragraph 5 - page 232, paragraph 1 *	5	
A	IBM TECHNICAL DISCLOSURE BULLETIN. vol. 20, no. 3, August 1977, NEW YORK US page 950 G.A. DEIGHTON 'STEAM AND WAFER CLEANING' * the whole document *	5	
A	US-A-4 261 791 (RCA CORP.) * claim 1 *	5	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 24 SEPTEMBER 1993	Examiner VANCRAEYNST F.H.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : Intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons A : member of the same patent family, corresponding document	

EPO FORM 1503 01.92 (P0601)



European Patent  
Office

EP 92 11 8561

### CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing more than ten claims.

- ☐ All claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for all claims.
- ☐ Only part of the claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims and for those claims for which claims fees have been paid.
- namely claims:
- ☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims.

### LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirement of unity of invention and relates to several inventions or groups of inventions.

namely:

See Sheet B.

- ☒ All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.
- ☐ Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid.
- namely claims:
- ☐ None of the further search fees has been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims.
- namely claims:





European Patent  
Office

EP 92 11 8561 -B-

#### LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirement of unity of invention and relates to several inventions or groups of inventions, namely:

1. Claims 1-4,6 : Treatment of a waste solution issuing from the cleaning of a silicon mass.
2. Claim 5 : Treatment of the silicon mass itself after cleaning.